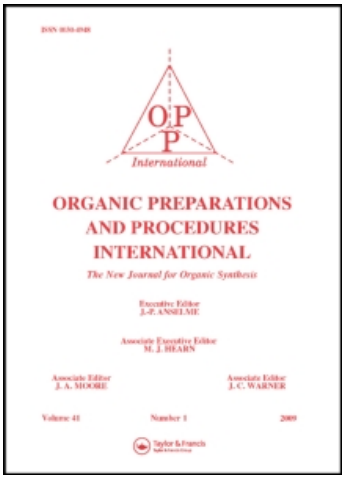


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# A ONE-STEP PREPARATION AND HETERO-DIELS-ALDER DIMERIZATION OF 2-PHENYLPROPENAL

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## A ONE-STEP PREPARATION AND HETERO-DIELS-ALDER DIMERIZATION OF 2-PHENYLPROPENAL

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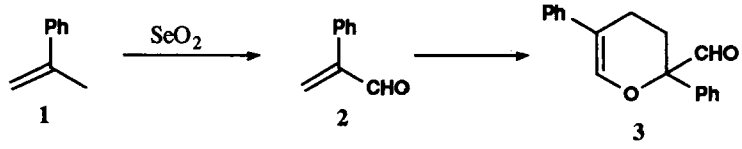
Atropaldehyde (2-phenylpropenal, **2**) is claimed to be an exocrine secretion compound of white cabbage butterfly *(Pieris rapae crusivora)*[1] and of ponerine and myrmicine ants.[2] The formation of **2** in the thermal degradation of polystyrene[3] and its reported instability under normal conditions led us to investigate its preparation and transformations.

The preparation of **2** was first reported in 1968.[4] Gas-phase catalytic oxidations of 2-phenylpropene (**1**)[5] is a patented process and the effects of various catalysts and reaction parameters have been studied recently.[6] Among laboratory scale methods,[7,8] the one reported by Crossland is adequate though involving three steps. We used the well-known ability of selenium dioxide to oxidize allylic positions[9] and obtained **2** in 44% yield from **1** in a 3 hrs reaction and distillation procedure.[10] Our method is rapid, uses less steps and gives a yield comparable to that of Crossland. Benzene turned out to be more suitable as a solvent than 1,4-dioxane or acetic acid.

Based on NMR and MS spectral evidence, it was found that **2** dimerizes to give a new pyran derivative, 2,5-diphenyl-2-formyl-3,4-dihydro-2H-pyran (**3**), *via* a hetero Diels-Alder reaction. HPLC




1 2 3

analysis under gradient elution conditions showed that the dimeric product contained 93% of **3**. Both the reaction itself and the selectivity are known reaction modes of α,β-unsaturated aldehydes.[11]

## EXPERIMENTAL SECTION

NMR spectra were recorded on a Joel JMN-FX 200 FT spectrometer. High resolution mass spectra were obtained on a Finnigan MAT 8200 instrument. Chemical shifts (δ) are in parts per million relative to TMS. HPLC experiments were performed with a Hewlett-Packard HP 1090A HPLC with Rheodyne 7010/7012 injector (5-µl loop), a built in diode array detector (DAD), HP 85B computer control, HP 3392A integrator, HP 9121 disc memory and HP ColorPro plotter. Analysis was performed on a 250 x 4.0 mm i.d. LiChrosorb Hibar 5-µm RP-18 column (Merck). A 25-min linear gradient from 50% methanol/water to 100% methanol at a flow rate of 1.0 mL/min was used. The column temperature was 50°. The mobile phase components were HPLC-grade methanol (LiChrosolv from Merck) and distilled deionized water which was further purified with Gelman's Water I apparatus. Solvents were filtered through a 0.45 µm membrane filter before use and degassed during use with a constant flow of helium. The dimeric product **3** was dissolved in methanol. The concentration of working solution was about 80 ng/µl. The detection wavelength was 260 nm. The on-line UV spectrum from 190-400 nm was recorded for **3** with the diode array detector (DAD) at the eluent composition at which it eluted in the chromatographic run. The UV spectrum showed absorption maxima at 206 and 262 nm.



**2-Phenylpropenal (2).**- A mixture of distilled 2-phenylpropene (**1**) (Merck, 17.73 g, 0.15 mol), selenium dioxide (20.00 g, 0.18 mol) in benzene (250 mL) was refluxed for 3 hrs. The reaction mixture was decanted while hot to remove selenium and benzene was distilled off. The residue was fractionated twice under reduced pressure using a 30-cm Vigreux column, and the fraction bp. 77-82°/1 mmHg was collected to give 8.73 g (44%) 2-phenylpropenal as a partly solid material. The product was stored below 0°, since it dimerizes at room temperature. The purity was checked by $^1$H NMR ($CDCl_3$): δ 9.61 (s, 1H, CHO), 7.62-7.42 (aromatic protons), 6.59 (s, 1H) and 6.14 (s, 1H, $=CH_2$). $^{13}$C NMR ($CDCl_3$): δ 193.4 (CHO), 147.9 (=C), 136.9 ($=CH_2$), 133.4, 128.7, 128.3, and 128.0 (aromatic carbons).

**2,5-Diphenyl-2-formyl-3,4-dihydro-2H-pyran (3).**- Enal (**2**), when stored at room temperature, dimerizes in 1-2 hrs quantitatively affording the pyran derivative **3** as a viscous oil. $^1$H NMR ($CDCl_3$): δ 9.55 (s,1H, CHO), 7.48-7.23 (m, 11H, aromatic protons and =CH), 2.67-2.12 (m, 4H, $CH_2$). $^{13}$C NMR ($CDCl_3$): δ 199.7 (CHO), 140.8 (=CH-O), 138.3, 136.4, 128.8, 128.5, 128.1, 126.5, 125.6 and 124.4 (aromatic carbons), 114.9 (=C), 84.3 (C-O), 27.9 and 20.3 ($CH_2$).

**MS analyses. 2-Phenylpropenal (2).**- EI/MS, 70 eV, *m/z* (%): 132 (52, $M^+$), 104 (48, $C_8H_8$), 103 (100, $C_8H_7$), 102 (10, $C_8H_6$), 78 (10, $C_6H_6$), 77 (45, $C_6H_5$). CI/MS (isobutane), *m/z* (%): 133 (100, $MH^+$), 105 (8, $MH^+$-$CH_2O$). The EI mass spectrum of **2** shows two characteristic fragmentation patterns for the molecular ion. The loss of the formyl group forms *m/z* 103, and *m/z* 77 is indicative of the phenyl group in the molecule. The CI spectrum of **2** shows the protonation at the aldehyde group

following the loss of $CH_2O$ from protonated molecule producing the ion *m/z* 105.

HRMS Calcd. for $C_9H_8O$: 132.0575. Found: 132.0576

**2,5-Diphenyl-2-formyl-3,4-dihydro-2H-pyran (3).**- EI/MS, 70 eV, *m/z* (%): 264 (50, $M^+$), 236 (60, $C_{17}H_{16}O$), 235 (100, $C_{17}H_{15}O$), 132 (30, $C_9H_8O$), 118 (30, $C_9H_{10}$), 115 (50, $C_9H_7$), 105 (90, $C_7H_5O$), 104 (80, $C_8H_8$), 103 (80, $C_8H_7$), 91 (50, $C_7H_7$), 77 (75, $C_6H_5$), 51 (35, $C_4H_3$). CI/MS (isobutane), *m/z* (%): 265 (100, $MH^+$), 247 (25, $MH^+$-$H_2O$), 235 (15, $MH^+$-$CH_2O$), 133 (50, MH+-$C_8H_9O$). The primary fragmentation routes of **3** under electron ionization are the loss of CO and CHO from the molecular ion. The formation of hydrocarbon ion products $C_6H_5^+$, $C_7H_7^+$, $C_8H_8^+$, $C_9H_7^+$, $C_9H_9^+$ and oxygen containing ions $C_7H_5O^+$ and $C_9H_8O^+$ are diagnostic for the structure of **3**. The CI-spectrum of the protonated dimer **3** shows typical losses of neutral groups like $H_2O$ (247) and $CH_2O$ (235). The protonated monomer (*m/z* 133) is also present.

HRMS Calcd. for $C_{18}H_{16}O_2$: 264.1151. Found: 264.1171.

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